

SCIENCE FOR CERAMIC PRODUCTION

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SPONTANEOUSLY DECOMPOSING ELECTROSMELTING SLAG IN THE PRODUCTION OF CERAMIC TILES

A. I. Nestertsov,¹ T. S. Rudenko,¹ and E. N. Lutsenko¹Translated from *Steklo i Keramika*, No. 9, pp. 13–15, September, 2002.

A mixture composition for facing ceramic tiles is developed based on spontaneously decomposing high-base electrosmelting slag. The physicomechanical properties of fired tiles meet the requirements of GOST 6141–91.

In recent years the ceramic industry in Russia has experienced difficulties regarding the supply of raw materials. Supplies of refractory and high-melting clays from Ukraine, perlite from the Caucasus, and other materials from the former USSR territories have dropped. Development of new deposits of minerals, as a rule, involves substantial capital investments. Therefore, using technogenic waste is more cost-effective and can simultaneously solve two problems: the problem of environmental protection and that of sourcing materials.

The development of material-saving technologies in construction ceramics is based on replacement of traditional imported materials by local clays and industrial waste. Metallurgical slag and ash are among the most space-taking among industrial byproducts, being inferior in volume only to waste generated by the mining industry.

The purpose of the present study is the development of mixture compositions and technology for ceramic tiles intended for interior decoration of walls based on high-basicity electrosmelting spontaneously decomposing slag generated by the Oskol'skii Electrometallurgical Works (OEMW) to be produced at the Construction Materials and Household Equipment Company, which is part of the Oskol'skii Electrometallurgical Works (city of Staryi Oskol).

The process of formation of low-shrinkage anorthite and wollastonite structures for ceramic tile mixtures using calcium-containing slag has great scientific and practical significance. The important factors in these mixtures are the composition, structure, and properties of carbonate materials and the value of the alkaline-earth modulus $RO : R_2O$ [1].

The considered mixtures included spontaneously decomposing electrosmelting slag, local low-melting clay, sand, and Latnenskoe semi-acid clay as the corrective additive

with respect to the Al_2O_3 content. Chemical composition of starting raw materials is presented in Table 1.

The hydraulically cooled electrosmelting slag from the Oskol'skii Works is highly base slag, which, as a consequence of decomposition of silicate, transforms into disperse powder with a particle size up to 5 μm and a specific surface area of 3800 cm^2/g . The basicity modulus of the slag is over 2. According to the data of x-ray phase and differential-thermal analysis, $\gamma-2CaO \cdot SiO_2$ prevails in the slag composition. Helenite, mervinite, rankinite, and magnoferrite are present as well. The presence of endothermic effects on the DTA curve at temperatures of 320, 700, and 800°C and the weight loss on the TG curve point to the presence of hydrates in the slag composition.

The local low-melting Gorodishchenskoe clay has a brown color. The prevailing argillaceous materials are nontronite and hydromica, and a small quantity of kaolinite, which is confirmed by the x-ray phase analysis data. The presence of nontronite in the clay is indicated by the endothermic effects on the DTA curve at 180, 580, and 770°C. Gorodishchenskoe clay in its mineral composition belongs to the montmorillonite group. The impurities in clay are carbonates, free quartz, and organic inclusions. The clay is acid with a high content of Fe_2O_3 ; its plasticity number is 10.

The prevailing argillaceous minerals in the semi-acid clay LT-3 from the Latnenskoe deposit are kaolinite and montmorillonite, which is confirmed by the DTA and the x-ray phase analysis data. Its impurities include hydromica, feldspar, free quartz, and iron compounds. The clay is finely disperse, plastic, and has high binding capacity. The high content of alumina in the presence of alkali metal oxides expands the temperature interval of sintering.

The alkali-bearing additive was the waste generated by the Vyshnevogorskii Feldspar Concentration Works. The

¹ Belgorod State Technological Academy of Construction Materials, Belgorod, Russia.

TABLE 1

Material	Mass content, %								calcination loss
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	
Slag from Oskol'skii Works	21.55	6.47	—	12.93	43.10	15.95	—	—	—
Clay:									
LT-3	60.73	25.38	1.71	0.99	0.39	0.29	0.37	0.35	9.79
Gorodishchenskoe	66.25	11.86	0.78	4.73	1.21	2.45	1.09	4.39	7.24
Sand	99.97	—	—	0.03	—	—	—	—	—
Nepheline-feldspar concentrate	64.35	21.45	—	0.31	0.82	—	5.62	7.45	—

waste contained microcline, albite, plagioclase, nepheline, biotite, hornblende, etc.

The development of mixture composition proceeded from the fact that solid phase reactions in calcium-bearing mixtures take place at temperatures of 800–1000°C and lead to the formation of a calcium aluminosilicate material of the anorthite type, which makes it possible to obtain articles with high mechanical strength and low shrinkage. The emergence of calcium silicate in firing is not excluded, which leads to a decrease in shrinkage and partly to decreased mechanical strength of ceramics.

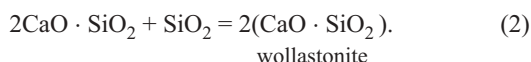
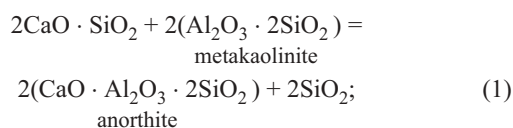
The use of the laws of thermodynamics in the analysis of the solid-phase processes makes it possible to determine the direction of the reaction, to identify the emerging compounds, to calculate the thermal balance of processes, etc. Such estimates can be carried out by calculating the variation of the standard Gibbs energy of solid-phase reactions using the fundamental ratio:

$$\Delta G_T^0 = \Delta H_T^0 - T \Delta S_T^0,$$

where ΔG_T^0 is the variation of the isobaric-isothermic potential, kJ/mole; ΔH_T^0 is the variation of the enthalpy, kJ/mole; T is the temperature, K; ΔS_T^0 is the variation of the entropy, kJ/mole.

The fundamental possibility of any reaction is determined by the value of ΔG_T^0 . The most probable of all possible processes will be the one accompanied by the highest loss of ΔG_T^0 .

The formation of anorthite and wollastonite in ceramic mixtures using metallurgical slag is possible due to reactions between bicalcium silicate contained in the slag and the products of disintegration of argillaceous minerals and free silicon oxide.



The calculated values of ΔG_T^0 in the formation of anorthite according to reaction (1) and wollastonite according

to reaction (2) within a temperature range of 300–1100°C vary from –357.46 to –412.66 and from –54.99 to –58.14 kJ/mole, respectively. This suggests that the formation of anorthite in the presence of argillaceous material is preferred compared to the formation of wollastonite that is synthesized from bicalcium silicate and free SiO₂. However, the variation of ΔG_T^0 of wollastonite is evidence of its thermodynamic stability within the temperature range up to 1100°C.

In developing compositions and studying the properties of fired samples with the anorthite structure, we proceeded from the fact that the molar ratio of oxides in anorthite was equal to CaO : Al₂O₃ : SiO₂ = 1.00 : 1.85 : 2.15. Taking into account the chemical composition of the initial components, the determining oxide in the calculation of the considered composition is aluminum oxide, since its content in the components is significantly lower than that of other oxides. The excessive content of CaO and SiO₂ in the mixture does not exclude the formation of wollastonite and other components in firing.

Since the mixtures were synthesized not from pure oxides but from components containing the initial oxides as part of different compounds, the ratio of argillaceous components in the considered ceramic compositions varied, whereas the content of the electrosmelting slag remained constant and amounted to 50%. The content of low-melting clay in the mixtures varied from 40 to 20%, and that of refractory clay changed from 10 to 30%.

Samples shaped as tiles (50 × 50 × 6 mm) and bars (60 × 18 × 6 mm) were molded at a unit pressure of 22 MPa from powder of 6% moisture obtained by drying the slip and its subsequent milling to grains of size below 0.63 mm. The bending strength of the samples after molding was 1.1 MPa. The slip with moisture 43% and efflux time 13 sec measured on an Engler viscosimeter was prepared by joint wet milling of the components in a ball mill for 1 h. After drying, the samples experienced fast firing, the firing lasted 20 min, and the maximum firing temperature varied within an interval of 1000–1080°C.

It was found that samples of all compositions fired in the interval of 1000–1080°C had bending strength more than 15 MPa and water absorption of 18–21%, which meets the GOST 6141–19 requirements for facing tiles made of car-

bonate-containing materials. As for firing shrinkage, it virtually does not vary for compositions containing low-melting clay fired in the interval of 1000 – 1080°C and amounts to 0.58%. Partial replacement of low-melting clay with high-melting clay increases shrinkage from 0.58 to 1.15%, which points to a modification of the sintering process.

The sufficiently high bending strength of samples containing up to 40% low-melting nontronite clay with a minimum shrinkage of 0.58 – 0.66% and an insignificant increase in water absorption in firing is evidence of predominantly solid-phase sintering and the formation of new crystalline phases that form a solid skeleton. The emergence of anorthite is accompanied by an increase in volume, which impedes shrinkage. X-ray phase analysis data indicated the total absence of initial bicalcium silicate in the composition of the fired tiles and the presence of new crystalline formations of anorthite, helenite, and wollastonite.

Partial replacement of non-sintering low-melting clay by kaolinite-hydromica high-melting sinterable Latnenskoe clay LT-3 modifies the sintering process, which is manifested as water absorption decreasing from 20.04 to 18.29%, shrinkage increasing from 0.58 to 1.15%, and bending strength growing from 16.6 to 20.1 MPa. Kaolinite is partly mullitized in firing, the formation of aluminocalcium silicate decreases, and the quantity of alkaline-earth melt becomes higher.

Thus, the formation of a low-shrinkage structure of facing tiles with properties meeting the requirements of GOST 6141–91 based on electromelting highly basic, spontaneously decomposing slag depends on the content of low-melting and high-melting clay in the mixture. A content of low-melting clay up to 40% facilitates the formation of the low-shrinkage anorthite structure.

We investigated the effect of the formation of wollastonite on the structure and properties of the material on mixtures based on electromelting slag and sand taken in the ratio of 7 : 3 equal to the theoretical ratio of CaO to SiO₂ in wollastonite. For binding and obtaining the required strength in molded samples, high-melting clay LT-3 was introduced into the mixtures in the amount of 20 – 30%. Samples containing 20% clay after molding had insufficient strength and after firing in the interval of 1000 – 1080°C did not reach the bending strength of 15 MPa. An increase in the content of the clay LT-3 up to 30% made it possible to obtain samples whose bending strength was 16 – 17 MPa, water absorption 20.4%, and shrinkage 0.65 – 0.70%. According to the x-ray phase analysis data, kaolinite partly becomes mullitized in firing, and wollastonite, helenite, and anorthite are formed. In the presence of an alkaline-earth melt, a less strong wollastonite structure is formed. The presence of the high-temperature modification of bicalcium silicate is registered.

Introduction of an additional 20% of low-melting clay, which contains up to 40% free quartz, into a mixture containing 20% LT-3 clay and the respective decrease of the amount of free quartz make it possible to significantly increase the strength of molded samples up to 1.2 MPa, to lower the fire

shrinkage to 0.5%, and to increase the bending strength up to 18.0 – 18.5 MPa with an insignificant increase in water absorption (up to 21.3%). An increase in the bending strength and a decrease in shrinkage show that the activity of silica plays a deciding role in the transformation of bicalcium silicate into wollastonite and other silicates.

The effect of alkaline-earth melt on the process of transformation of bicalcium silicate into wollastonite and other aluminosilicates was investigated on compositions with additional introduction of the nepheline-feldspar concentrate from the Vyshnevogorskoe deposit in the amount of 10 and 20% while preserving the slag : sand ratio equal to 7 : 3, which is needed for the transformation of bicalcium silicate into wollastonite. Introduction of 10% feldspar concentrate into the mixture composition provides for the formation of a low-shrinkage mixture with an insignificant increase in water absorption from 19.74 to 20.25% and bending strength from 16.0 – 17.2 to 17.5 – 18.1 MPa after firing in the temperature interval of 1050 – 1080°C. Introduction of 20% feldspar concentrate into the mixture composition increases shrinkage from 0.50 to 0.74%, decreases strength to 14.87 MPa, and lowers water absorption to 19.64%.

Evidently, an increase in the quantity of the liquid phase primarily facilitates a fuller transformation of bicalcium silicate into other calcium silicates and aluminosilicates, and a stronger structure is formed as a consequence of a direct contact between the emerging crystalline phases. A substantial increase in the liquid phase content leads to the contact of crystalline phases via the liquid phase, which facilitates the transition to liquid-phase sintering. This is manifested in increased shrinkage and decreased water absorption and strength. In this case the alkaline-earth modulus should amount to 16.31 – 24.30. It is established that bicalcium silicate in the presence of low-melting clay and feldspar concentrate is fully transformed into other compounds, whereas in their absence a high-temperature modification of bicalcium silicate is registered in the wollastonite composition.

A wollastonite composition containing up to 50% electromelting slag, as well as sand and low-melting and high-melting clays was selected for further study. The estimated values of coordination between the glaze and ceramics were determined from the TCLE using the Winkelman and Schott method. These values were $6.3 \times 10^{-6} \text{ K}^{-1}$ for ceramics and $5.2 \times 10^{-6} \text{ K}^{-1}$ for the glaze used at the Oskol'skii Construction Materials and Household Equipment Company. The glaze on the surface of the samples after firing showed no cracks, crackle, or flaking.

The moisture expansion of ceramics after autoclave treatment was 0.01%, which does not exceed the prescribed limit of 0.03%. The estimated and experimental values show good agreement between the TCLE of the glaze and ceramics, which is necessary for long-time service of tiles.

Semi-industrial production of facing tiles was carried out using molding powder obtained under laboratory conditions with subsequent molding of tiles sized 150 × 75 × 6 mm on a

hydraulic press in the laboratory of the facing tile division of the Oskol'skii Construction Materials and Household Equipment Company and firing and glazing on the production line of this division. The resulting facing tiles fully met the requirements of GOST 6141–91.

Thus, low-shrinkage mixtures for facing tiles of the anorthite and wollastonite compositions based on highly basis spontaneously decomposing electrosmelting slag from the

Oskol'skii Electrometallurgical Works have been developed and tested under industrial conditions.

REFERENCES

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